



## Water quality improvement of a lagoon containing mixed chemical industrial wastewater by micro-electrolysis-contact oxidization\*

Ya-fei ZHOU<sup>†1</sup>, Mao LIU<sup>1</sup>, Qiong WU<sup>2</sup>

<sup>1</sup>College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China)

<sup>2</sup>The Eleventh Design & Research Institute of IT, Co., Ltd, Dalian Office, Dalian 116600, China)

<sup>†</sup>E-mail: nkzhouyf@gmail.com

Received June 30, 2010; Revision accepted Nov. 26, 2010; Crosschecked Apr. 20, 2011

**Abstract:** A lagoon in the New Binhai District, a high-speed developing area, Tianjin, China, has long been receiving the mixed chemical industrial wastewater from a chemical industrial park. This lagoon contained complex hazardous substances such as heavy metals and accumulative pollutants which stayed over time with a poor biodegradability. According to the characteristics of wastewater in the lagoon, the micro-electrolysis process was applied to improve the biodegradability before the bioprocess treatment. By the orthogonal experimental study of main factors influencing the efficiency of the treatment method, the best control parameters were obtained, including pH=2.0, a volume ratio of Fe and reaction wastewater of 0.03750, a volume ratio of Fe and the granular activated carbon (GAC) of 2.0, a mixing speed of 200 r/min, and a hydraulic retention time (HRT) of 1.5 h. In the meantime, the removal rate of chemical oxygen demand (COD) was up to 64.6%, and NH<sub>4</sub><sup>+</sup>-N and Pb in the influent were partly removed. After the micro-electrolysis process, the ratio of biochemical oxygen demand (BOD) to COD (B/C ratio) was greater than 0.6, thus providing a favorable basis for bioprocess treatment.

**Key words:** Memetic algorithm (MA), Neural network (NN) learning, Back propagation (BP), Extremal optimization (EO), Levenberg-Marquardt (LM) gradient search, Basic oxygen furnace (BOF)

doi:10.1631/jzus.A1000304

Document code: A

CLC number: X506

### 1 Introduction

A wastewater lagoon in the New Binhai District, a high-speed developing area, Tianjin, China covers approximately 2.5–2.6 square kilometers, with an average depth of 2 m, and a storage volume of about 5 million cubic meters. For over 30 years, the wastewater lagoon has been receiving a great deal of household sewage as well as wastewater with poor biodegradability from chemical industry park, leading to an increasingly serious long-term pollution. In particular, water quality in the lagoon became worse

than class V, the lowest level of the National Environmental Quality Standards for Surface Water, which means that water in the lagoon is unsuitable for agricultural use, and the lagoon has basically lost its self-purification capacity. The analytical results indicated that the main pollution factors involved are chemical oxygen demand (COD) and NH<sub>4</sub><sup>+</sup>-N, and hazardous substances detected were heavy metals and organic pollutants such as pesticides. As an important threat to human health, this wastewater lagoon has also hampered the development of economy and society in the surrounding areas. Thus, it is urgent and quite meaningful to develop an economical and practical technology to treat wastewater from this wastewater lagoon.

In recent years, the development of wastewater treatment technologies has greatly improved water

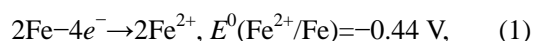
\* Project supported by the National Natural Science Foundation of China (No. 70833003), and the National Science and Technology Support Project of 11th 5-Year Plan, China (No. 200603746006)  
© Zhejiang University and Springer-Verlag Berlin Heidelberg 2011

quality, and reduced the cost of treatment processes (Scholz and Fuchs, 2000; Zakkour *et al.*, 2001; Dhoub *et al.*, 2003; 2006). However, treatment and remediation of some wastewater lagoons receiving mixed chemical industrial wastewater with high toxicity and poor biodegradability is still an intractable problem to be solved (Ellouze *et al.*, 2009). The ferrite process can be an effective technology in treating wastewater with poor degradability, but it has hardly been used in remediation of a lagoon due to its high cost (Pérez *et al.*, 2002; Lou *et al.*, 2009). Although membrane bioreactors have been successfully applied to treat industrial wastewater over the past decade (Acharya *et al.*, 2004; Kurian *et al.*, 2006), the membranes can easily be defiled when used in mixed industrial wastewater treatment (Geng and Hall, 2006; Nghiem and Hawkes, 2007). Traditional activated sludge and its modified technology are of low cost and are widely used in wastewater treatment; however, many wastewater lagoons contain hazardous materials from industrial production, which can inhibit the bioactivity of living organisms and reduce the removal efficiency of toxic pollutants. In recent years, more and more attention has been paid to electrochemical methods for industrial wastewater treatment. In particular, electrolysis has been the most frequently used unit process because of its rapid reaction rate, high efficiency, and low sludge production. However, the high level of energy consumption limits its further application and leads to the development of interior micro-electrolysis in wastewater treatment (Jin *et al.*, 2003).

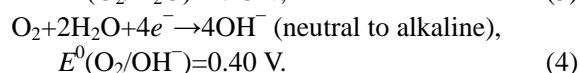
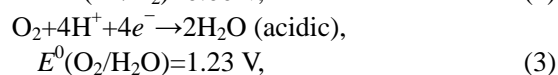
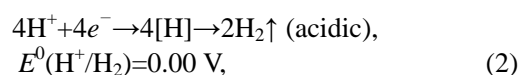
Micro-electrolysis also referred to as iron chip filtration has been used to pretreat industrial wastewater due to its extensive adaptability to wide variations of composition of wastewater (Yang *et al.*, 1997). Its effects on treatment of poor biodegradable wastewater, including pesticide (Wu *et al.*, 2003), pharmacy (Liu *et al.*, 2008), and dye wastewaters (Cheng *et al.*, 2005), have been studied. The iron and carbon materials casted into the container can form numerous microscopic galvanic cells, where the electrons are supplied from the galvanic corrosion of iron (anode) (Zhou and Fu, 2001; Cheng *et al.*, 2007). Products released from the galvanic cell reaction include hydroxyl, atomic hydrogen, and  $\text{Fe}^{2+}$ , which have high activities to decompose contaminants (Li *et al.*, 2004; Wang *et al.*, 2008). In addition, some pol-

lutants can also be removed by electrophoresis and adsorption (Han, 1991; Yang *et al.*, 1997). Furthermore, interior micro-electrolysis pretreatment is of low cost and effective because it does not require chemical coagulants and external power in the cases of coagulation and electrolysis (Xu *et al.*, 2003).

The half-cell reactions can be represented as oxidation in the anode:



and reduction in the cathode:



where  $E^0$  is the standard electrode potential, and  $[\text{H}]$  is the hydrogen atom density.

Recently, micro-electrolysis has been widely used in the treatment of wastewater from dye-stuffs (Wang *et al.*, 2001), petrochemical (Zhu *et al.*, 2004), and electroplating industries (Dai, 2005). This method can improve the biodegradability of wastewater (Wu *et al.*, 2009), because it can damage the chromophoric groups ( $-\text{NO}_2$  and  $-\text{NO}$ ) of organic pollutants and break off the double bonds of unsaturated groups (Li *et al.*, 2004). Besides, metals behind iron in the metal moveable order regulation and other metal ions and chemicals, which have stronger oxidizabilities, would be deoxidized to products with lower toxicity levels (Yang *et al.*, 1997; Wang *et al.*, 2008).

## 2 Materials and methods

### 2.1 Raw wastewater

The raw wastewater samples used in this study were taken from a wastewater lagoon in an industrial zone of Tianjin, China (Fig. 1). Some parameters of water quality were listed in Table 1.

### 2.2 Materials

Waste iron scraps were obtained from a mechanical processing plant in Tianjin, China, and the

iron particles (0.90–1.95 mm) were bought from a chemical reagent company in Tianjin, China. Iron scraps and particles were first degreased in a NaOH solution (10%, w/w) for 10 min, and then soaked in a diluted sulfuric acid solution (5%, w/w) for 20 min to remove the surface oxidation film and increase reaction activities. Finally, it was cleaned by deionized water with two or three repetitions.

The granular activated carbon (GAC) with the particle size of 0.65–1.04 mm was washed with water for two or three times before use.

### 2.3 Experimental procedure

According to a certain ratio, processed iron scraps and GAC were put to a beaker of 1 L, and then 800 ml wastewater (pH regulated) was poured into the beaker and stirred continuously with a mixer. Because

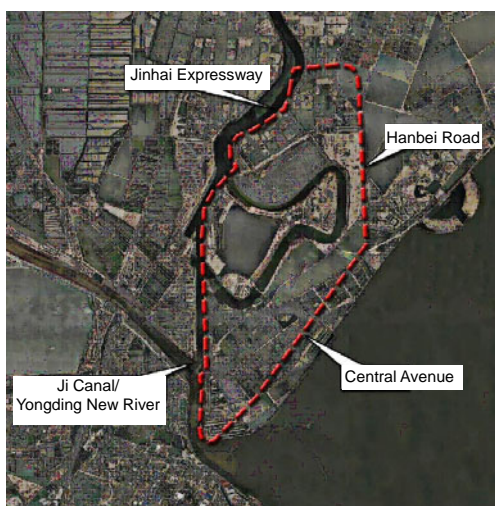


Fig. 1 Wastewater lagoon containing mixed chemical industrial wastewater

of the high salinity (Table 1), the wastewater samples could work as an electrolyte, and thus promote the micro-electrolysis process. After a certain time of mixing and reaction, pH was regulated to 8.5 with NaOH solution, and aerated for 30 min. After sedimentation, the supernatant fluid was fetched out and the water quality was analyzed. The schematic of the process was shown in Fig. 2.

First, the orthogonal experiment was used to optimize the experiment design, and the influences of different parameters on treatment efficiency were tested. Parameters chosen were pH in reaction beaker, volume ratio of Fe and reaction wastewater ( $V(\text{Fe})/V$ ), volume ratio of Fe and GAC ( $V(\text{Fe})/V(\text{C})$ ), mixing speed, and hydraulic retention time (HRT) (Xu *et al.*, 2003). The orthogonal experiment arrangement was listed in Table 2.

Once the optimum condition was identified through the orthogonal experiments, a separate experiment was carried out under the same condition, while dissolved oxygen (DO) and pH were detected at an interval of 10 min through out the whole micro-electrolysis process, and each detection was made by performing three parallel tests.

Table 2 Orthogonal experiment arrangement  $L_{16}(4^5)^*$

Level	Factor				
	a	b	c	d	e
1	2	0.01875	0.5	150	0.5
2	3	0.02500	1	200	1
3	4	0.03125	1.5	250	1.5
4	5	0.03750	2	300	2

\*  $L_{16}(4^5)$  means 5 factors with 4 levels. a: pH; b:  $V(\text{Fe})/V$ ; c:  $V(\text{Fe})/V(\text{C})$ ; d: mixing speed (r/min); e: hydraulic retention time (HRT, h)

Table 1 Water quality situation of experimental raw wastewater

COD (mg/L)	BOD (mg/L)	$\text{NH}_4^+-\text{N}$ (mg/L)	Pb (mg/L)	Total dissolved solid (mg/L)	Chloride (mg/L)	Salinity (%)	Chroma	pH
327.93–353.41	2.7–15.0	29.90–32.18	0.14–0.19	15 623	7480	1.1	50 (celadon)	5.4

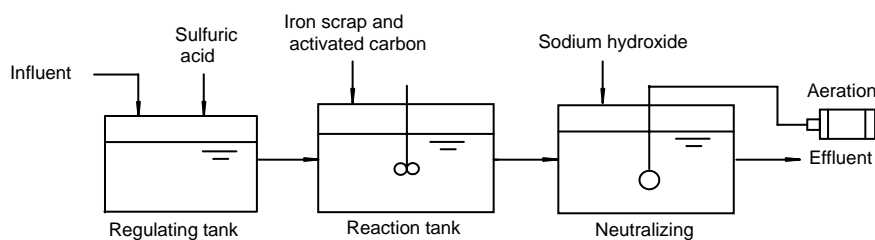


Fig. 2 Technological flow diagram of the micro-electrolysis process

Due to limits of the experiment scale, another group of experiments composed of 12 parallel tests was made under exact the same conditions as the above DO and pH experiments. Twelve beakers were back-filled with the same wastewater, iron scraps, and GAC; the 12 parallel tests started at the same time by 12 synchronal mixers. Wastewater of 20 ml was sampled from each beaker at each 10-min interval from 0 to 90 min to avoid disturbance to the micro-electrolysis process. Samples from 12 beakers at the same time were then mixed together in a 250 ml beaker as a time-tagged sample. These 10 time-tagged samples were used as influents and pH was regulated to 8.5 with NaOH, and then these samples were aerated for half an hour. After sedimentation, the supernatant fluids were fetched out and water quality was analyzed, including COD, biochemical oxygen demand (BOD),  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ , and Pb.

## 2.4 Analytical methods

Water quality was analyzed referring to the standard methods for examination of water and wastewater (State Environmental Protection Administration of China, 2002). COD, chroma, and salinity were determined by the potassium dichromate method, the visual colorimetry, and a hand-held refractometer manufactured by the Xingchenguang Optical Instruments Factory (Chengdu, China), respectively. DO, pH,  $\text{NH}_4^+\text{-N}$ , and BOD were analyzed using an HQ-10 DO detecting instrument manufactured by HACH Company (USA), the PB-10 pH instrument of Sartorius Company (Germany), the Nessler's reagents spectrophotometer using a UV-Vis Spectrophotometer (WD-9403D, Beijing, China), and an LY-05 rapid detection equipment manufactured by Lv Yu Environmental Protection Co., Ltd. (Qingdao, China), respectively. Pb was determined by the flame atomic absorption using a flame atomic absorption spectrophotometer (AA240FS, Varian, USA). The volumes of scrap iron and GAC were measured with a graduated cylinder.

## 3 Results and discussion

### 3.1 Filtration of optimum conditions

The program and results can be seen in Table 3.  $K_{ij}$  was the sum of COD removal efficiency  $k_{ij}$  in the  $i$ th level ( $i=1, 2, 3, 4$ ) of factor  $j$  ( $j=a, b, c, d, e$ ), and  $k_{ij}$

was the average of  $K_{ij}$ .  $R_j = \max\{k_{1j}, k_{2j}, k_{3j}, k_{4j}\} - \min\{k_{1j}, k_{2j}, k_{3j}, k_{4j}\}$  (Table 3). The larger  $R$  value was, the larger the effects of factors on the index were, and the largest  $R$  value showed the main affecting factor of the experiment (Zhu *et al.*, 2009). The results of orthogonal experiment showed that  $R$  values of five different factors on COD removal efficiency were:  $R_a=35.96 > R_d=13.08 > R_c=10.47 > R_b=9.32 > R_e=3.78$ . It can be concluded that factor a (pH), factor d (mixing speed), and factor c ( $V(\text{Fe})/V(\text{C})$ ), had greater influence on the COD removal rate, while factor b ( $V(\text{Fe})/V$ ) and factor e (HRT) had less influence.

The relationship between COD removal efficiency and levels of each factor can be seen in Fig. 3. According to preliminary analysis, the optimum program was a1, b4, c4, d2, and e3, and the corresponding conditions included pH=2.0,  $V(\text{Fe})/V=0.03750$  (the volume of influent was 800 ml),  $V(\text{Fe})/V(\text{C})=2.0$ , mixing speed=200 r/min, and HRT=1.5 h. The following verification experiment showed that COD in the effluent under the optimum conditions was 121.6 mg/L, and the removal efficiency of COD was up to 64.6%, which was better than the best result of the 16 orthogonal experiments (Exp. 4 in Table 3). Chroma in the effluent was quite low, which was not originally celadon, but appeared a little yellow because of a small amount of  $\text{Fe}^{3+}$  contained in the water.

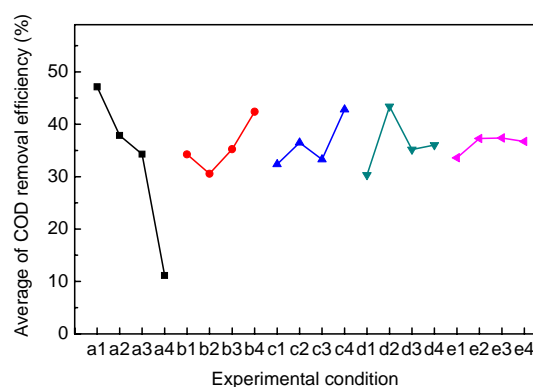


Fig. 3 Relationship between experimental conditions and COD removal efficiency

pH was the main factor on COD removal efficiency by micro-electrolysis ( $R=35.96$ ), which was three times greater than the second most important factor ( $R=13.08$ ). A part of wastewater in the lagoon was from the dye industry, and the presence of  $\text{H}^+$  can cause a deoxidation reaction with chromophoric

**Table 3** Calculated results of orthogonal experiments  $L_{16}(4^5)$ 

Exp. No.	Level of different factors					COD removal Efficiency (%)
	a	b	c	d	e	
1	1	1	1	1	1	32.72
2	1	2	2	2	2	52.42
3	1	3	3	3	3	43.24
4	1	4	4	4	4	60.1
5	2	1	2	3	4	35.56
6	2	2	1	4	3	31.73
7	2	3	4	1	2	38.61
8	2	4	3	2	1	45.56
9	3	1	3	4	2	30.17
10	3	2	4	3	1	34
11	3	3	1	2	4	37.07
12	3	4	2	1	3	35.92
13	4	1	4	2	3	38.59
14	4	2	3	1	4	14.06
15	4	3	2	4	1	22.07
16	4	4	1	3	2	27.89

Factor	COD removal efficiency (%)								
	$K_{1j}$	$K_{2j}$	$K_{3j}$	$K_{4j}$	$k_{1j}$	$k_{2j}$	$k_{3j}$	$k_{4j}$	$R_j$
a	188.48	151.46	137.16	102.61	47.12	37.86	34.29	11.16	35.96
b	137.04	132.21	140.99	169.47	34.26	33.05	35.25	42.37	9.32
c	129.41	145.97	133.03	171.3	32.35	36.49	33.26	42.82	10.47
d	121.31	173.63	140.69	144.07	30.33	43.41	35.17	36.02	13.08
e	134.35	149.09	149.48	146.79	33.59	37.27	37.37	36.7	3.78

Optimum condition: a1, b4, c4, d2, e3

$K_{ij}$ : sum of COD removal efficiency in the  $i$ th level ( $i=1, 2, 3, 4$ ) of factor  $j$  ( $j=a, b, c, d, e$ );  $k_{ij}$ : average of  $K_{ij}$ ;  $R_j=\max\{k_{1j}, k_{2j}, k_{3j}, k_{4j}\}-\min\{k_{1j}, k_{2j}, k_{3j}, k_{4j}\}$ . Levels of different factors (a, b, c, d, e) are indicated in Table 2

groups in the wastewater; therefore, as the initial pH increased, the removal efficiency of chroma decreased. Besides, the oxygen electrode potential  $E$  ( $O_2/H_2O$ )=1.23 V, which is higher in acidic medium than that in neutral medium, and also low pH can increase the oxygen electrode potential, and accelerate and enhance the electrode reaction (Eq. (3)).

Mixing speed was an important factor affecting pollutant removal only in modified micro-electrolysis, which was reacted in a container by a mixer. The greatest contact of iron scraps with GAC would be observed with a proper mixing speed, while pollutants could be mostly removed. When the mixing speed was too slow, iron scraps and GAC would be submerged at the bottom of the beaker, thus limiting the formation of micro cells. When the mixing speed was too high, pollutants and reaction products that had adsorbed or deposited on the surface of GAC would be transported back to water by the strong hydraulic effect.

$V(Fe)/V(C)$  was another important factor in the micro-electrolysis. A certain ratio of carbon can not only accelerate erosion of iron scraps but also increase pollutant removal. But too much carbon would restrain the electrode reaction, and pollutants would be mostly removed through adsorption.

After the orthogonal experiment, waste iron scraps and iron particles of the same volume were placed into two beakers separately, and were tested in the optimum condition to find out what was better suited for wastewater treatment. Almost all of the iron particles were submerged in the bottom of the beaker when the mixing speed was less than 200 r/min, and most iron particles were still submerged in the bottom even at a mixing speed of 300 r/min. The analysis of COD in both effluents showed that removal efficiency of COD with iron particles was almost half of that with iron scraps, which was 29.54%. The scraps were flake-shaped, which had larger specific surface areas

than those of iron particles. Besides, the scraps were lighter than particles, and thus it could easily be stirred by the mixer. Contact of GAC with wastewater was increased, and the removal efficiency of pollutants could be improved. Considering the adverse effects of iron particles as well as the cost of iron particles, the waste iron scraps from mechanical processing plant were recommended in the treatment process to realize the direct use of waste.

### 3.2 Influences of DO and pH on the removal efficiency of COD

Under the optimum conditions, three parallel experiments were conducted to investigate the changes of DO and pH for each 10 min interval through the whole reaction process. The average values of the parallel tests were depicted in Fig. 4. As shown in Fig. 4, DO decreased quickly at the beginning of the tests when cathode reaction was expressed as

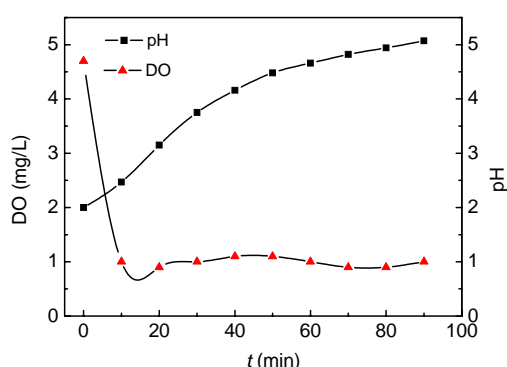
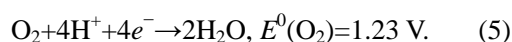
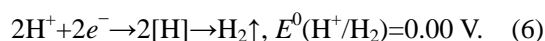


Fig. 4 Changes of DO and pH in the whole micro-electrolysis reaction phase

The corrosion reaction was the fastest since the greatest potential difference between the anode and the cathode occurred. After that, the wastewater was kept at a low DO level (about 1.0 mg/L) until the reaction proceeded to completion when cathode reaction took place as follows:



[H] generated in the reaction had high activities, which could damage the chromophoric groups of pollutants and break down macromolecules into small molecules. Thus, the biodegradability of the effluent

was enhanced, and the chroma of wastewater was basically removed.

Under the optimum conditions, two beakers containing the same wastewater were treated separately with and without aeration, and the effluents were analyzed. Results showed that the removal efficiency of COD with aeration was 43.8%, which was lower than that without aeration. In the aerobic condition, reduction ability of the reaction system was restrained by too much  $\text{O}_2$  contained in the water sample, and in the same time, flocculation was enhanced. The proper DO value was different when wastewater was treated differently. As a result, it can be concluded that the lower DO had the obvious advantage in the removal of COD in this kind of wastewater.

pH increased from 2.0 to more than 5.0 through the whole micro-electrolysis reaction process. The oxygen electrode potential was 1.23 V in acidic medium, which was higher than that in the neutral medium. It can be inferred that a low pH level was superior for electrode reaction. As pH was increased, the electron acceptor was reduced, thus resulting in a decrease in the treatment efficiency (Li and Wang, 2003).

The concentration of  $\text{H}^+$  quickly decreased in the initial phase and slowed after 40 min. As shown in Fig. 4, it can be concluded that reduction reaction was the main factor in the pollutant removal. As the concentration of  $\text{H}^+$  decreased, the reduction reaction slowed in the late stage.

### 3.3 Treatment efficiency of micro-electrolysis

Under the optimum conditions, the effluents at different times were collected and analyzed to explore the removal mechanisms of pollutants, in which a group of experiments composed of 12 parallel tests were made. Changes in the concentration of COD,  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ , and Pb in the effluents were determined and depicted in Figs. 5–7.

The concentration of COD quickly decreased in the initial 40 min, and then increased slowly during 40 to 70 min, and finally decreased after 70 min. COD was quickly removed in the first 40 min, which coincides with the pH increase in Fig. 4, and the proposed idea that COD was removed mainly through reduction reaction in the initial 40 min was confirmed. After 40 min, the reduction reaction was weakened,

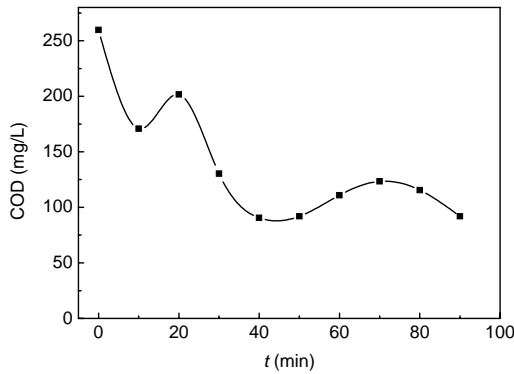


Fig. 5 Removal efficiency of COD by micro-electrolysis in an operation cycle

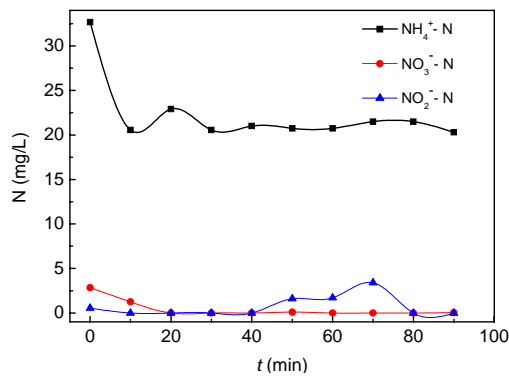


Fig. 6 Change of N in an operation cycle

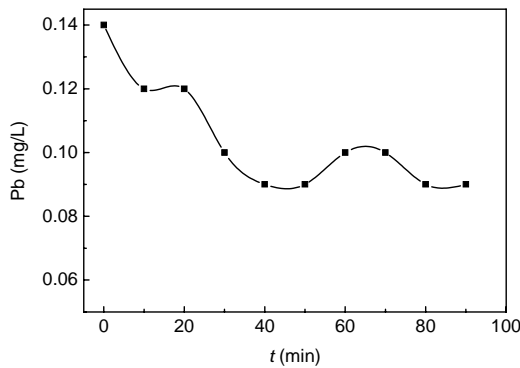


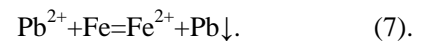
Fig. 7 Change of Pb in an operation cycle

COD was removed through electrophoresis, adsorption, flocculation, and other reactions. When pH increased to 1, flocculation played a more important role in COD removal.  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  generated during the reaction could attach to the surface of iron scraps and GAC, and impede the process of electrode reaction, resulting in a decrease in the removal efficiency of COD. On the other hand, pol-

lutants attached to the surface of iron scraps and GAC continued to adsorb and desorb during the mixing process, which resulted in the fluctuation of COD values.

As shown in Fig. 6,  $\text{NH}_4^+\text{-N}$  was removed mainly at the initial 10 min. From then on, the concentration of  $\text{NH}_4^+\text{-N}$  had been fluctuating between 20.0–23.0 mg/L. The removal efficiency of  $\text{NH}_4^+\text{-N}$  mainly depends on the oxidation reaction and the adsorption process. From Fig. 4, it can be seen that a rapid decrease of DO occurred in the first 10 min, and was then maintained at a low level until the end. Thus, it can be speculated that the removal of  $\text{NH}_4^+\text{-N}$  may be related to the concentration of DO. At the initial 10 min, oxidation dominated in the wastewater treatment reaction. However, after 10 min, adsorption played a more important role. The concentrations of  $\text{NO}_3^-\text{-N}$  and  $\text{NO}_2^-\text{-N}$  in the influent were very low during the 20 to 40 min period. After 40 min, the concentration of  $\text{NO}_2^-\text{-N}$  got a small increase. After 80 min, it turned to 0 again. Thus, it can be concluded that the removal of  $\text{NO}_3^-\text{-N}$  and  $\text{NO}_2^-\text{-N}$  from wastewater basically depends on the adsorption process.

In the micro-electrolysis reaction, the removal of  $\text{Pb}^{2+}$  mainly depends on redox and adsorption.  $\text{Pb}^{2+}$  in the anode can react with iron as shown in the following reaction:



Pb generated from the reaction was adsorbed by iron and GAC, or deposited with  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$ ; thus, it can be removed from wastewater. Because the adsorption was a reversible process,  $\text{Pb}^{2+}$  and Pb continued to adsorb or desorb from the surface of iron and GAC, thus leading to the fluctuation in the concentration of Pb in wastewater.

### 3.4 Improvement in biodegradability of wastewater by micro-electrolysis

Under the optimum conditions, COD, BOD,  $\text{NH}_4^+\text{-N}$ , and Pb in the influent and effluent were detected, and the results were listed in Table 4. After the micro-electrolysis reaction, the removal efficiency of Pb reached 31.6%, thus leading to a lower toxicity.  $\text{Fe}^{3+}$  generated in the reaction could enhance the activity of microorganisms in the following

biotreatment unit, and changed the structure of the sludge particles, which improved the simultaneous nitrification and denitrification processes (Liu *et al.*, 2008). As this work was aimed at the removal of COD and the improvement of wastewater biodegradability, less attention was paid to the removal of Pb. However, a higher Pb removal rate may be attained through regulation of parameters in micro-electrolysis (Xiao *et al.*, 2009).

**Table 4 Improvement of wastewater biodegradability**

Parameter	Concentration (mg/L)		Removal rate (%)
	Influent	Effluent	
pH	5.4	5.7	
NH <sub>4</sub> <sup>+</sup> -N	31.3	20.69	33.9
Pb	0.19	0.13	31.58
COD	343.26	121.55	64.59
BOD	4.3	74	–
<i>B/C</i> ratio	0.013	0.609	–

*B/C* ratio: ratio of BOD to COD of wastewater

The ratio of BOD to COD (*B/C* ratio) of wastewater had been greatly increased. Moreover, Cl<sup>-</sup> contained in wastewater can form Cl, Cl<sub>2</sub>, and ClO<sup>-</sup>, which can degrade organic pollutants in an indirect manner (Chiang *et al.*, 1995; Ribordy *et al.*, 1997). Meanwhile, redox during the micro-electrolysis process can turn some poor biodegradable pollutants into biodegradable ones, and toxic substances into less toxic ones, resulting in the increase of *B/C* ratio in the effluent, thus providing foundation for follow-up bioprocesses.

## 4 Conclusions

The micro-electrolysis method is feasible to treat wastewater with low COD and high toxicity. Iron scraps used in the reaction had larger specific surface areas and less weights than iron particles, and thus they had a higher COD removal efficiency. Also, they could be obtained from mechanical processing plant to realize the direct use of waste.

The optimum conditions of reaction in this study included pH=2.0,  $V(\text{Fe})/V=0.03750$  (the volume of influent was 800 ml),  $V(\text{Fe})/V(\text{C})=2.0$ , mixing speed=200 r/min, and HRT=1.5 h. Under the conditions, the concentration of COD in the effluent decreased to 121.6 mg/L with a COD removal efficiency

of 64.6%. Almost all of the chroma could be removed by micro-electrolysis.

pH was the main factor on COD removal efficiency by micro-electrolysis, and mixing speed and  $V(\text{Fe})/V(\text{C})$  also had significant influences on the COD removal rate.

Oxygen electrode potential  $E$  (O<sub>2</sub>/H<sub>2</sub>O) was higher in an acidic medium than that in a neutral medium, and low pH could increase the oxygen electrode potential, and accelerate and enhance the electrode reaction, leading to a high COD removal efficiency.

Under the low DO condition, the cathode generated a large number of H<sub>2</sub>, which was good for the removal of COD in wastewater. Treatment without aeration had better efficiency than that with aeration.

The micro-electrolysis treatment had a certain removal efficiency of NH<sub>4</sub><sup>+</sup>-N and Pb. After treatment, the *B/C* ratio of wastewater increased from 0.013 to 0.609, biodegradability was far enhanced, and thus the effluents could flow directly into follow-up bioprocesses.

## References

- Acharya, C., Nakhla, G., Bassi, A., Kurian, R., 2004. Treatment of high strength pet food wastewater using two-stage membrane bioreactors. *Water Environment Research*, **78**(7):661-670. [doi:10.2175/106143006X99812]
- Cheng, C.C., Hu, D.W., Zhou, J.X., 2005. Study on the process of dyestuff wastewater treated by microelectrolysis. *Chemistry and Bioengineering*, **22**(1):29-30 (in Chinese).
- Cheng, H.F., Xu, W.P., Liu, J.L., Wang, H.J., He, Y.Q., Chen, G., 2007. Pretreatment of wastewater from triazine manufacturing by coagulation, electrolysis, and internal microelectrolysis. *Journal of Hazardous Materials*, **146**(1-2):385-392. [doi:10.1016/j.jhazmat.2006.12.038]
- Chiang, L.C., Chang, J.E., Wen, T.C., 1995. Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. *Water Research*, **29**(2):671-678. [doi:10.1016/0043-1354(94)00146-X]
- Dai, X.L., 2005. Study on the treatment of chromium-containing wastewater of galvanization by utilizing the technology of micro-electrolysis and its application. *Industrial Water Treatment*, **25**(1):69-71 (in Chinese).
- Dhouib, A., Hamad, N., Hassairi, I., Sayadi, S., 2003. Degradation of anionic surfactants by *Citrobacter braakii*. *Process Biochemistry*, **38**(8):1245-1250. [doi:10.1016/S0032-9592(02)00322-9]
- Dhouib, A., Aloui, F., Hamad, N., Sayadi, S., 2006. Pilot-plant treatment of olive mill wastewaters by *Phanerochaete chrysosporium* coupled to anaerobic digestion and ultrafiltration. *Process Biochemistry*, **41**(1):159-167. [doi:10.1016/j.procbio.2005.06.008]



- Ellouze, M., Saddoud, A., Dhoubi, A., Sayadi, S., 2009. Assessment of the impact of excessive chemical additions to municipal wastewaters and comparison of three technologies in the removal performance of pathogens and toxicity. *Microbiological Research*, **164**(2):138-148. [doi:10.1016/j.micres.2006.11.007]
- Geng, Z., Hall, E.R., 2006. Characterization of fouled membranes from a membrane enhanced biological phosphorus removal system. *Water Science & Technology*, **54**(10):169-176. [doi:10.2166/wst.2006.707]
- Han, H.J., 1991. Industrial wastewater treatment by micro-electrolysis. *Environmental Protection*, **1**:17-18 (in Chinese).
- Jin, Y.Z., Zhang, Y.F., Li, W., 2003. Micro-electrolysis technology for industrial wastewater treatment. *Journal of Environmental Sciences*, **15**(3):334-338.
- Kurian, R., Nakhla, G., Bassi, A., 2006. Biodegradation kinetics of high strength oily pet food wastewater in a membrane-coupled bioreactor (MBR). *Chemosphere*, **65**(7):1204-1211. [doi:10.1016/j.chemosphere.2006.03.050]
- Li, C., Xia, J., Wang, Y.Z., 2004. Micro-electrolysis process for treating dyeing wastewater. *Journal of Nanjing Forestry University (Natural Sciences Edition)*, **28**(1):87-88 (in Chinese).
- Li, D.S., Wang, B.S., 2003. Pretreatment of high concentration organic chemical wastewater by aerated Fe/C micro-electrolysis. *China Water & Wastewater*, **19**(10):58-60 (in Chinese).
- Liu, G.X., Cheng, A.H., Wang, Z.Y., 2008. Research on enhanced biological nitrogen removal by micro-electrolysis method. *Chinese Journal of Environmental Engineering*, **2**(7):927-931 (in Chinese).
- Lou, J.C., Huang, Y.J., Han, J.Y., 2009. Treatment of printed circuit board industrial wastewater by Ferrite process combined with Fenton method. *Journal of Hazardous Materials*, **170**(2-3):620-626. [doi:10.1016/j.jhazmat.2009.05.020]
- Nghiem, L.D., Hawkes, S., 2007. Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): mechanisms and role of membrane pore size. *Separation and Purification Technology*, **57**(1):176-184. [doi:10.1016/j.seppur.2007.04.002]
- Pérez, M., Torrades, F., Domenech, X., Peral, J., 2002. Fenton and photo-Fenton oxidation of textile effluents. *Water Research*, **36**(11):2703-2710. [doi:10.1016/S0043-1354(01)00506-1]
- Ribordy, P., Pulgarin, C., Kiwi, J., Peringer, P., 1997. Electrochemical versus photochemical pretreatment of industrial wastewater. *Water Science & Technology*, **35**(4):293-302. [doi:10.1016/S0273-1223(97)00038-3]
- Scholz, W., Fuchs, W., 2000. Treatment of oil contaminated wastewater in a membrane bioreactor. *Water Research*, **34**(4):3621-3629. [doi:10.1016/S0043-1354(00)00106-8]
- State Environmental Protection Administration of China, 2002. Methods for the Examination of Water and Wastewater Analysis. China Environmental Science Press, Beijing, China (in Chinese).
- Wang, M.X., Zhu, S.Q., He, X.W., 2001. Study on micro-electrolysis treatment for decolorizing dyed water. *Journal of China University of Mining & Technology*, **11**(2):212-216 (in Chinese).
- Wang, X.Q., Hu, X.M., Shen, X., 2008. Study on treatment for dyeing wastewater by iron-carbon micro-electrolysis and A/O process. *Industrial Safety and Environmental Protection*, **34**(7):22-25 (in Chinese).
- Wu, H.F., Kong, H.L., Wang, S.H., 2003. Study on pretreatment of agricultural pesticide wastewater by micro-electrolytic method and Fenton reagent oxidation method. *Techniques and Equipment for Environmental Pollution Control*, **4**(2):18-21 (in Chinese).
- Wu, Q., Zhou, Q.X., Hua, T., 2009. Development of micro-electrolysis and its combined process for refractory wastewater. *Technology of water treatment*, **35**(11):27-32 (in Chinese).
- Xiao, T.T., Han, Y.H., Jin, D., Zhang, L., 2009. Removal of lead from PAC through micro-electrolysis. *Liao Ning Chemical*, **38**(1):11-14 (in Chinese).
- Xu, D.H., Li, D.S., Wang, Z.P., 2003. Research on the treatment of coking plant wastewater by the process of aeration micro-electrolysis. *Water Purification Technology*, **19**(10):58-60 (in Chinese).
- Yang, J., Lu, Z.Y., Hu, J.C., Gu, X.S., 1997. Status and prospects of technology for antibiotics industrial wastewater treatment. *Environmental Science*, **18**(3):83-85 (in Chinese).
- Zakkour, P.D., Gaterell, M.R., Griffin, P., Gochin, R.J., Lester, J.N., 2001. Anaerobic treatment of domestic wastewater in temperate climates: treatment plant modeling with economic considerations. *Water Research*, **35**(17):4137-4149. [doi:10.1016/S0043-1354(01)00145-2]
- Zhou, G.P., Fu, D.F., 2001. Application and development for micro-electrolysis technology. *Techniques and Equipment for Environmental Pollution Control*, **2**(4):18-24 (in Chinese).
- Zhu, X.B., Zhou, J.T., Qiu, J.S., 2004. A pilot-plant study of applying micro-electrolysis process to reuse of effluent from petroleum refinery. *Environmental Engineering*, **22**(2):7-9 (in Chinese).
- Zhu, S., Hua, T., Zhou, Q.X., Wu, Q., 2009. Ecological safety regulation of A/DAT-IAT process for municipal wastewater treatment. *Chinese Journal of Applied Ecology*, **20**(5):1209-1213 (in Chinese).